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The importance of adsorption in igneous partitioning of trace elements

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Abstract—For accurate mathematical modeling of trace-element partitioning during igneous fractionation, adsorption should be considered. Because of adsorption, the partitioning of elements between liquid and a surface layer of a crystal is often not the same as the partitioning between liquid and the solid crystal at true equilibrium. In some minerals, e.g. high-calcium pyroxene, the effect of adsorption during crystal growth may be very important; this is suggested by the frequent occurrence of sector zoning in augite, and the wide range in measured partition coefficients for such elements as rare earths. The ions which are enriched by adsorption are usually those which are favored substituents according to Goldschmidt's rules. In other minerals, uptake of trace elements may be closer to equilibrium partitioning, rather than being determined by kinetic factors. For example, the relative partitioning of REE, U, Th and Pb into feldspars is qualitatively predicted by Pauling's rules for complex ionic crystals, rather than by Goldschmidt's rules.

INTRODUCTION

A NUMBER of factors are presently considered to influence the partitioning of trace elements during igneous fractionation, including the charge and size of ions (GOLDSCHMIDT, 1937), their electronegativity (RINGWOOD, 1955a), the formation of complexes (RINGWOOD, 1955b), and for transition metals, crystal-field effects (BURNS, 1973). There is no unifying theory or set of rules to take care of all possible cases, however, and the partitioning of each element must be carefully considered to determine which of the factors is dominant (SHAW, 1953).

Modern mathematical treatments of igneous fractionation usually do not require a detailed rationale for the observed partitioning, but rely instead on empirically-derived partition coefficients. The use of such coefficients usually assumes at least a temporary form of equilibrium, even if the process being modelled is fractional crystallization. It is the purpose of this paper to discuss a phenomenon, namely adsorption, which probably causes these models to be inaccurate in certain important cases. It is instructive to consider adsorption in light of some of the crystal-chemical factors mentioned above. Two important mineral examples, pyroxene and feldspar, will be discussed.

HIGH-CALCIUM PYROXENE— INCORPORATION BY ADSORPTION

It was suggested by DEVORE (1955) that incorporation of trace elements is often dominated by adsorption, that is adherence of ions or atoms to the surface of crystals or other solids. He suggested that most such adsorbed atoms would eventually be incorporated into defects of one sort or another in a crystal, rather than into regular sites. Perhaps because

Devore discussed mainly metamorphic examples, and because more recent studies have generally found that trace elements substitute into regular sites of crystals (e.g. MORRIS, 1975), the process of adsorption has since been neglected as a factor in igneous fractionation, although its importance in sedimentary environments is well established (PARKS, 1975; BERNER, 1975).

A type of adsorption rather different from that suggested by Devore has been proposed to account for sector zoning in minerals. In the models of NAKAMURA (1973) and DOWTY (1976), an important determinant of the composition of sectors (segments of the crystal which have grown under different faces) is the nature of the partially completed cation sites, or protosites, exposed on the surfaces of the growing crystal. Foreign cations are presumed to substitute into these protosites in place of the normal occupants. The older model of HOLLISTER (1970) and HOLLISTER and GANCARZ (1971) relies on somewhat different premises, but it also can be described as an adsorptive model. A salient feature of all these models is that they describe a non-equilibrium situation, in that the interior of the crystal is not necessarily in equilibrium at any time with the growth medium. Indeed, the existence of sector zoning demonstrates non-equilibrium between the crystal and the growth medium for at least some sectors. One may postulate that there is a temporary "surface equilibrium" between the growth medium and the adsorption layer on the crystal surface, but the distribution of elements between growth medium and surface is generally not the same as that between growth medium and the interior of the crystal at true equilibrium; if this were not the case, most types of sector zoning would not exist. Each face or surface must establish its own specific surface-layer composition.

The nature and quantity of adsorbed cations has

traditionally been considered to be a function of some of the crystal-chemical attributes mentioned in the introduction. In particular, for elements which are dominated by ionic behavior, considerations of charge and size of the ions are most important. Accordingly, in a model for sector zoning which seems to be successful in essentially all of the cases examined (DOWTY, 1976), it was found necessary to postulate that the preferences for occupancy of favorably exposed protosites are essentially as given by Goldschmidt's rules; i.e. smaller, more highly charged cations are favored over normal occupants of a site, within reasonable ionic size limits. In cases in which the ions are not spherical (transition metals), or in which the covalent nature of the bonding is dominant, hard and fast rules for adsorption are more difficult to establish, but the general principle is simply that atoms which can bond more strongly to the surface are favored. These atoms are not necessarily those which are the most stable in the interior of the crystal.

Perhaps the best-known example of sector-zoning is titanaugite, an igneous mineral in which hour-glass structure is very common. The sector zoning in this mineral involves sectoral variations in the incorporation of Ti, Fe^{3+}, and Al into the octahedrally coordinated M1 site, with charge compensation provided by substitution of Al for Si in the tetrahedral site. In such coupled substitutions, incidentally, it appears that the dominant factor is the substitution in the more weakly bonding site (in this case, M1). It is usually only the sites with relatively weak bonds which are exposed on the surface for any length of time, and which presumably have an opportunity to pick up foreign cations by adsorption.

The influence of adsorption on the partitioning of these elements into pyroxene thus seems well established. It may be deduced, furthermore, that other elements which have not yet been studied in detail will also be affected. Although some geochemically important elements like rare earths probably do not substitute into the M1 site in augite, but rather the larger M2 site, it seems quite possible that they could displace the normal M2 occupant, Ca, by virtue of their higher charge.

If the partitioning of elements into high-calcium pyroxene during igneous crystallization is significantly influenced by adsorption, it is predicted that the concentrations of elements which are favored substituents according to Goldschmidt's rules will be enriched in the crystal by a process of rapid (fractional) crystallization, as opposed to a strict equilibrium process. Sectoral variations in these elements is also expected; the sectors which have grown under the {100} form are normally most enriched in Ti, etc., in titanaugites, and are also predicted to be most enriched in "foreign" M2 site substituents. Of all forms in the crystal, {100} has the most favorable type of protosites (NAKAMURA, 1973; DOWTY, 1976).

The data presently available are not sufficient to test these predictions thoroughly, although they establish a pattern of wide variability in some of the elements presumably affected, for example rare-earths. Measured crystal–liquid partition coefficients for rare-earths vary by over a factor of ten. ZIELINSKI and FREY (1974) found that solid–vapor partition coefficients for Gd in diopside were about ten times as large when the diopside crystallized during the experiment as when crystals were present beforehand. CULLERS et al. (1973) derived diopside–liquid partition coefficients for rare earths from supposed equilibrium experiments, and found values at the low end of the range for natural specimens. There are several plausible explanations for these variations aside from adsorption, including incomplete separation of crystals and matrix, effects due to diffusion limitations in the liquid, and other possibilities discussed by the above authors. Very likely several factors are involved in any case, and it is impossible to say which is most important without further measurement and experiment. However, the existence of sector zoning in igneous minerals, and the undoubted importance of adsorption in determining compositions of minerals grown from aqueous solution (BERNER, 1975) make it imperative that adsorption be considered as one of the variables.

FELDSPAR—TRUE EQUILIBRIUM PARTITIONING

Pauling's rules for the architecture of complex ionic crystals (PAULING, 1960) deal with the same considerations of ionic charge and size as Goldschmidt's rules. However, the predictions of the two sets of rules can be quite different. Although geochemists are more accustomed to think of trace element partitioning in terms of Goldschmidt's rules, some cases are actually better described by Pauling's rules. The partitioning of several elements into feldspars is an important example.

In framework silicates, the replacement of a silicon by aluminium introduces a bonding deficiency on the two adjacent oxygen atoms, as well as an overall charge imbalance. According to Pauling's electrostatic valence rule (his second rule), this bonding deficiency is 1/4 valence units. Such a deficiency is satisfied exactly by a calcium or other divalent atom in 8-coordination, as the bond strength given up by a cation is its charge divided by its coordination number. Smaller divalent cations, such as Mg, which take 6-coordination, or cations with higher charge evidently would provide too great a bond strength to the oxygen atom, hence are discriminated against. It is thus found that, with a couple of exceptions, framework silicates do not contain small or highly charged cations as major constituents, except aluminum and silicon in tetrahedral sites. This analysis is given by PAULING (1960). An additional reason for preference for large cations by the framework structures is that a high degree of polymerization of tetrahedral cations

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The well-known and geochemically important europium "anomaly" of feldspars (PHILPOTTS and SCHNETZLER, 1968; WEIL and DRAKE, 1973) is evidently a function of these crystal-chemical factors. The large divalent europium ion is readily admitted into the feldspar structure, while the smaller trivalent rare earths are excluded. The minute amounts of trivalent rare earths which are found in feldspar apparently do not occur in regular sites (MORRIS, 1975). Goldschmidt's rules incorrectly predict exactly the opposite, or a negative europium anomaly in feldspar. The equally important partitioning of uranium and thorium vs lead in feldspars is explained in the same way; the larger divalent lead ion is admitted, while the smaller quadrivalent uranium and thorium are rejected, again in contradiction to Goldschmidt's rules. The fact that the smaller more highly charged ions may be more likely to form stable complexes in the liquid could contribute to the observed behavior. However, it is unlikely that this is the sole cause; RINGWOOD (1955b) did not include RE^{3+}, Th^{4+} or U^{4+} among those ions which normally form complexes. Also, the same partitionings are found in metamorphic rocks.

Pauling's rules are intended to predict the ideal configuration of crystals, using minimum-energy considerations for a complete, solid crystal. Partitioning of elements is also influenced by their environment in the liquid, so we cannot say with certainty that the distribution of rare earths, uranium, lead, etc. in feldspars is a result of complete equilibrium between liquid and crystal. However, the fact that rules for completed crystals seem to be adhered to at least implies that adsorption is not likely to play an important role for these ions in feldspar. The reason that adsorption should apparently be so much less important in feldspar than pyroxene is unclear.

IMPLICATIONS FOR GEOCHEMICAL MODELING

An interesting implication of the contrast between the behavior of high-calcium pyroxene and feldspar is that in at least some cases Goldschmidt's rules describe the non-equilibrium process of adsorption and incorporation on crystal surfaces. The ideal configuration of a solid ionic crystal is certainly more properly described by Pauling's rules. This is not to say that in many cases the substitution of smaller or more highly charged cations into certain sites may not increase the stability of the crystal as a whole and thus influence partitioning, whether of major or minor elements. For example, the higher melting point of anorthite versus albite and resultant crystal–liquid partition coefficients for Ca and Na in the plagioclase series is undoubtedly a result of the higher charge of the calcium atoms (GOLDSCHMIDT, 1937). The difference between anorthite and albite is of

course a coupled substitution involving the tetrahedral sites as well as the large cations, but melting points are usually determined by the weakest bonds in the substance. Thus for true equilibrium conditions, as well as adsorption, the partitioning involved in a coupled substitution is expected to be dominated by the member of the pair which has the weaker bonds (in this case, the large cation and not the tetrahedral cation).

Pauling's second rule is not inviolable, since the bond strengths are a function of cation–anion distance as well as charge and coordination number (ZACHARIASEN, 1963), and it is apparent that in many cases its requirements are not so strict as to prevent Goldschmidt's rules from being applicable even to the case of true equilibrium. However, if a particular substitution in an ionic crystal satisfies Goldschmidt's rules and clearly violates Pauling's rules, this is good grounds for suspecting the influence of adsorption. When covalency and crystal field effects are important, predictions as to the importance of adsorption vs equilibrium are more difficult to make, but the general principle is the same; one must consider minimum energy configurations on the surfaces, as opposed to the interior of the crystal.

Goldschmidt's rules, and the other crystal-chemical considerations mentioned in the introduction, do not necessarily assume the existence of equilibrium. In fact, a competition between various atoms for crystal sites, which is often cited in justification of such rules, may suggest kinetic processes. However, the existence or nature of equilibrium between the liquid and crystal surfaces becomes of considerable importance in mathematical modeling of fractionation. Adsorption has not been explicitly considered in mathematical models for igneous fractionation, even when the emphasis has been on accounting for kinetic factors (e.g. ALBAREDE and BOTTINGA, 1972).

Mathematical models for dealing with adsorption do exist, however; an example is one developed by KRÖGER [1973, p. 11; a similar formulation is given by BRICE (1973), p. 125], in which the effective partitioning of a given element between crystal and melt is

$$K_{eff} = \frac{K + \alpha}{1 - [1 - \exp(-V\delta/D)][1 - K - \alpha]}$$

$$\alpha = (K_{ads} - K)\exp(-V_{sl}/V).$$

Here K is the equilibrium partition between solid (interior of the crystal) and liquid, K_{ads} is the partition coefficient adsorption-layer–liquid, V is the rate of growth, V_{sl} is the rate of transfer of foreign atoms between the crystal and the adjoining melt, D is the diffusion constant in the melt, and δ is the width of the diffusion boundary layer. One of the most interesting properties of this model is that K_{eff} reaches a maximum at intermediate growth rates if $K < 1$ and $K_{ads} > 1$; at very slow growth rates, $K_{eff} = K$, and at very fast rates $K_{eff} = 1$. In this respect, it is

different from an earlier model for increased non-equilibrium incorporation of trace elements originally developed by BURTON et al. (1953) which relies only on the establishment of a trace-element-enriched diffusional boundary layer (the effects of such a layer are included in the Kröger model). This earlier type of model, which has sometimes been suggested for geochemical partitioning (e.g. BOTTINGA et al., 1966; ALBAREDE and BOTTINGA, 1972), never predicts $K_{eff} > 1$, if $K < 1$. These different rate dependences, the frequent occurrence of sector zoning in the case of adsorption, and the existence of composition gradients in the liquid for the Burton et al. model may serve to differentiate the two models in practice.

In many geochemical situations the number and quality of the available data would not justify such a detailed model as Kröger's, although a test of the model may be feasible in some other specific instances. However, even if growth rates, etc. are unknown, it should be possible, and indeed necessary for very accurate results, to use different partition coefficients for certain minerals in different situations. In particular, the effective partition coefficients augite–liquid for trivalent rare-earths (not to mention Ti, Al, and Fe^{3+}) are probably higher for rapid crystallization than for equilibrium partial melting. Again, this is over and above any effect due to the establishment of a diffusional boundary layer.

SUMMARY AND CONCLUSIONS

1. When disequilibrium (kinetics) is a factor in igneous fractionation of trace elements, it may be permissible to model the process on the assumption that there is some type of equilibrium between the liquid, or a part of it, and a surface layer on the crystal. However, the equilibrium partition coefficient solid-crystal–liquid often does not accurately describe the composition of this surface layer because of adsorption. Such adsorption is probably especially important for high-calcium pyroxene (or at least certain faces thereof). If the growth rate and certain other parameters are known, adsorption can be modeled precisely; at the least, different partition coefficients may have to be used for crystallization as opposed to equilibrium melting.

2. It appears that Goldschmidt's rules for the behavior of trace element ions are applicable in some cases to adsorption, rather than a true equilibrium situation. At least, when a substitution obeys Goldschmidt's rules but violates Pauling's rules, this is grounds for suspicion that adsorption is involved.

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